

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
  - TEXT CUT OFF AT TOP, BOTTOM OR SIDES
  - FADED TEXT
  - ILLEGIBLE TEXT
  - SKEWED/SLANTED IMAGES
  - COLORED PHOTOS
  - BLACK OR VERY BLACK AND WHITE DARK PHOTOS
  - GRAY SCALE DOCUMENTS
- 

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problems Mailbox.**

1113.722



# PATENT SPECIFICATION

NO DRAWINGS

1113.722

Date of Application and filing Complete Specification: 12 May, 1965.

No. 20054/65.

Application made in United States of America (No. 369,277) on 21 May, 1964.

Complete Specification Published: 15 May, 1968.

© Crown Copyright 1968.

Index at acceptance:—C3 P(8A, 8D1A, 8D1B, 8D2A, 8D2B2, 8D3A, 8D5, 8D8, 8K8, 8K9, 8K11, 8P1C, 8P1D, 8P1E1, 8P1E2, 8P1E3, 8P1F, 8P1X, 8P3, 8P4C, 8P5, 8P6X, 11A, 11D2A, 11D8, 11K8, 11P1C, 11P1D, 11P1E1, 11P1F, 11P1X, 11P5, 11P6X, 13D3, 13G4X, 13H1, 13KX, 13N3, 13NX, 13Y)

Int. Cl.:—C 08 f 1/28, C 08 f 1/58

## COMPLETE SPECIFICATION

### Aerobically Polymerisable Compositions

We, MINNESOTA MINING AND MANUFACTURING COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of 2501 Hudson Road, Saint Paul, Minnesota 55101, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the polymerisation of acrylates and more particularly to aerobically polymerisable compositions comprising acrylate monomers and triaryl borane complexes the polymerisation of which can be initiated by free-radical catalysts.

Compounds containing ethylenic double bonds can be polymerised by peroxides. From United States Patent No. 2,985,633 it is known that certain boron-containing compounds when treated with oxygen also serve as catalysts for the polymerisation of ethylene under pressure. The presence of air or oxygen affects the speed of polymerisation of some polymerisation systems adversely, however, and sometimes entirely inhibits the reaction. In particular in systems where polymerisation occurs in the presence of much air or where the system is saturated by air in manipulation, as, for example, in dental applications or in the application of adhesives and sealants, this inhibitory effect is very disadvantageous since the polymerisation is generally unreliable or incomplete and special precautions have to be taken to provide essentially anaerobic conditions.

In accordance with the present invention when certain complexes of triaryl boranes are added to polymerisable mixtures of ethylenic monomers and free-radical catalysts, the resulting compositions are readily activated and form useful polymers even in the presence of air.

The present invention provides compositions which are activatable in the presence of a free radical catalyst to polymerise under aerobic conditions, the compositions including one or more mono- and/or bis-acrylate and/or methacrylate monomers having blended therewith from 0.05 to 6 percent by weight of the monomer or monomers of a triaryl borane complex (as hereinafter defined).

The invention also provides a process for initiating the aerobic free-radical polymerisation of such compositions by the step of heating the composition or adding acid to the composition to effect decomposition of the complex.

The compositions of the invention are useful as coatings (in the broadest sense, including adhesives) and many can also be employed as moulding, potting, embedding and sealing compositions.

The mono- and/or bis-acrylate and/or methacrylate monomers which are suitable for use in the compositions of the invention are those which are sensitive to air and/or oxygen and are normally polymerised with some difficulty, except in the almost complete absence of oxygen, when using free radical-forming initiators such as benzoyl peroxide, azo-bis-isobutyronitrile, and *t*-butyl hydroperoxide.

While it is possible to prepare compositions of the invention from the monomers as described above, presently preferred compositions are formed using monomers which are inhibited against polymerisation by their content of dissolved oxygen, but

[Price 4s. 6d.]

which do not dissolve further oxygen rapidly. Such monomers thus may be characterised by being normally sensitive to oxygen but not completely inactivated thereby, and are usually polymerisable under forcing conditions of elevated temperature and/or high catalyst concentration, particularly, where protected from acquisition of further dissolved oxygen, as for example by flooding the surface with an inert gas or, as in certain dental applications, covering with an oxygen impermeable cover of wax or sheeting.

A particularly valuable class of monomers are the bis-acrylate or bis-methacrylate esters of long chain alpha,omega glycols which have a structure between the hydroxyl groups not containing reactive substituents which would cause cross-linking before the compositions of the invention are cured.

Because the compositions of the invention are activated by acids they normally include only monomers which are neutral in reaction, or expressed differently, are free from acidic functional groups. They may include ester and amide groups. Copolymerisable acidic monomers are employed for particular purposes, however, in certain embodiments of the invention. Mixtures of monomers can be employed to produce copolymers, and low molecular weight prepolymers derived from such monomers can also be used. The larger bis-acrylate or bis-methacrylate terminated molecules may be considered as prepolymers since they are sometimes conveniently made by the reaction of glycidyl acrylate or methacrylate with a complex bisphenol or polyol.

The monomers employed in compositions of the invention include esters of acrylic and methacrylic acids, containing up to about 100 carbon atoms e.g. methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, *n*-butyl acrylate, allyl acrylate, 2-ethylhexyl acrylate, *n*-butyl methacrylate, fusel oil acrylate, hexyl methacrylate, octyl methacrylate, decyl methacrylate, lauryl methacrylate, or stearyl methacrylate, and di-functional esters including, for example, tetraethyleneglycol dimethacrylate, ethyleneglycol dimethacrylate, and bisphenol A bis(glycerylmono-methacrylate) ether as well as the bis-acrylates as described hereinbelow. Liquid mixtures of acrylate-type monomers which produce copolymers in conventional anaerobic free-radical polymerisation produce copolymers under aerobic conditions when employed in the compositions of the invention.

Examples of suitable free radical catalysts for inclusion in compositions of the invention are benzoyl peroxide, *t*-butyl hydroperoxide, azobisisobutyronitrile and methyl ethyl ketone peroxide.

The triaryl borane complexes which are incorporated in the compositions of the invention are represented by the general formula:



in which R represents an aryl radical having from 6 to 12 carbon atoms and Am represents sodium hydroxide, ammonia, benzene or an amine.

In some instances polymerisation appears to proceed to a highly cross-linked or insoluble state. This effect is particularly evident when certain compositions of the invention which contain oxirane groups are employed. Such compositions may include, e.g. glycidyl acrylate and/or methacrylate, either added as such or as the result of reaction of an excess thereof with a phenolic compound to give a bis-acrylate. The result appears to be formation of interpenetrating reticulate polymer molecules which seem to be mutually reinforcing as to the gross mechanical properties of the resultant polymers. In such compositions polymerisation of the monomer moieties possibly is induced by the free radical catalyst and triarylborane, while polymerisation of the oxirane moieties is induced simultaneously by the basic component of the nitrogenous complex, either as the free base or as the cation of the salt formed with the acid added to activate the composition.

The triaryl boranes employed are preferably those in which the aryl groups are free from interfering substituent groups such as hydroxyl, carboxyl and amino groups which would cause instability of the complex. However, groups such as halo, alkyl and alkoxy may be present as substituents in the aryl radicals. In general, all such triaryl boranes form complexes which are useful in compositions of the invention. It is presently preferred that complexes of simple unsubstituted triaryl boranes be used because they tend to be more readily soluble in the acrylate-type monomers and are more easily activated to induce polymerisation by heating or by acidification. Triphenyl borane complex is particularly convenient for these reasons.

Amines having up to about 20 carbon atoms and having pK values of 10 or less

may be used to complex the triaryl boranes. The amines are commonly unsubstituted but substituents such as the hydroxyl groups in ethanolamine and triethanolamine do not interfere, and such substituted amines may be used to form complexes. Ammonia, benzene and sodium hydroxide also form useful complexes with triaryl boranes and are considered the equivalents of amines for purposes of forming such complexes. The nitrogenous complexes which are readily activated (e.g. disassociated) either by heating or acidification are preferred.

Exemplary amines which form complexes useful in the compositions of the invention are listed in various classes as follows.

Alkylamines: methylamine, dimethylamine, trimethylamine, tri-*n*-butylamine, *n*-butylamine, hexylamine, octadecylamine, octylamine, dodecylamine, tetradecylamine, ethylamine, diethylamine, methylethylamine, methyl-*n*-butylamine, ethyl-*n*-butylamine, methyl-di-*n*-butylamine, *n*-propylamine, isopropylamine, tert-butylamine, diisopropylamine, triethylamine.

Cycloalkylamines: cyclohexylamine, dicyclohexylamine, 1,4-bis-methylamino-cyclohexane.

Aralkylamines: benzyl amine,  $\alpha$ -methyl benzylamine, *m*-xylylenediamine, *p*-xylylenediamine.

Polyamines: ethylene diamine, hexamethylene diamine, trimethylene diamine, diethylene triamine, triethylene tetramine.

Heterocyclic amines: pyridine, quinoline, pyrrolidine,  $\beta$ -picoline, piperidine, pipercolines, piperazine, lutidine, pyridazine, morpholine, *N*-methyl morpholine.

Also useful are certain substituted amines, e.g. ethanolamine, triethanolamine.

The triaryl boranes thus form base complexes with the complexing agents sodium hydroxide, ammonia, benzene, primary, secondary and tertiary alkylamines, cycloalkylamines and alkanol amines, primary aralkylamines and alkylene polyamines, and secondary and tertiary heterocyclic amines.

The amine complexes of triaryl boranes can be produced by the same methods employed by Brown et al., J. Am. Chem. Soc., Vol. 64, pg. 325 (1942) and vol. 67, pg. 374 (1945) for the formation of complexes of boron alkyls. These triaryl borane complexes may decompose very gradually at various rates on exposure to air, but they are relatively more stable and relatively safer to manipulate than the triaryl boranes from which they are made, especially those of higher molecular weight and those formed from the more basic amines and sodium hydroxide.

The triaryl borane-amine complexes are employed in compositions of the invention in amounts ranging from 0.05 percent to 6 per cent by weight based on the weight of the acrylate-type monomer, and usually from 0.5 to 1.0 percent by weight of the triaryl borane complex is presently preferred. The complex is added to the monomer before addition of the free radical catalyst.

The free radical catalysts, and in particular a peroxide catalyst, can be incorporated in compositions of the invention in amounts of from 0.01 percent to 5 percent based on the weight of the monomers. Amounts of from 2 to 5 percent based on the weight of the monomers are generally employed, but amounts of 0.01 to 2 percent are used with advantage when the composition is activated by an acidic monomer (such as methacrylic acid). These compositions are usually stable and storable for periods up to one year or more. Polymerisation of the compositions of the invention is induced by activation either by gentle heating or addition of an acidic starter.

Certain compositions of the invention contain from 0.5 to 2.0 percent by weight of oxirane oxygen, as is more fully illustrated hereinafter. The presence of the oxirane (or epoxy) groups represented by this content appears to enhance the adhesivity of cured compositions containing them even after prolonged exposure to moisture. The oxirane groups may be present in a monomer made by the reaction of an excess of e.g. glycidyl methacrylate with a phenolic material, such as bisphenol A, or they may be introduced into a monomer prepared by another route. It is found that it is advantageous in such compositions to provide a small additional amount of nitrogenous base, e.g. *N,N*-dimethyl-*p*-toluidine, in addition to any base in the triaryl borane-base complex. Such nitrogenous bases may be present in sufficient quantity in bismethacrylates or bisacrylates as impurity or a small amount may be added. It is desirable that the base be one which has a *pK* value of not more than 10 and a molecular weight of from 30 to 800 and be present in an amount of 0.5 to 2.0 percent by weight of the composition. Other suitable nitrogenous bases in addition to *N,N*-dimethyl-*p*-toluidine, for example, tri-*n*-butylamine, diethylene triamine, *N*-methyl piperidine, *N*-methyl morpholine, 2,5-dimethyl piperazine and 1,2,4-trimethyl piperazine. The

nitrogenous bases present appear to act in some manner as co-catalysts for polymerisation.

Many of the compositions of the invention are liquids at ordinary temperatures and pressures. However, if desired, organic solvents inert toward the initiator can be employed as diluents. For the purpose of producing sealants, adhesives, coatings, or other formulations for specific purposes, suitable compatible fillers, pigments, dyes, plasticizers, or other desired materials may also be added to the composition. Such adjuvants should be of neutral reaction, since acidic materials would initiate the polymerisation prematurely, and must also be unreactive with the free radical catalyst and/or triaryl borane complex.

For the preparation of the compositions of the invention, the monomer or mixture of co-monomers selected, (generally in more or less purified state, as accomplished e.g. by distillation in the case of lower molecular weight monomers), is mixed with any desired compatible solid or liquid adjuvant materials, such as pigments, dyes, plasticizers, or fillers. To this mixture is added the triaryl-borane complex, either directly or dissolved or suspended in a small amount of a solvent which, if desired, may be a copolymerisable monomer. After addition of the triaryl borane-complex, the desired free radical catalyst is added in suitable amount. As long as the components are free of any acidic monomers or co-monomers, the resulting composition is storable, as stated above, until activated by warming or acidification.

For prolonged shelf-life, and particularly where an acidic co-monomer is used, two component systems may be employed.

For such two component systems, the free radical catalyst and an acidic monomer may be dissolved separately in a small amount of suitable monomer to provide a second component. The first component includes the triaryl-borane complex and some monomer. The first component may include oxirane group-containing monomer when desired. Viscosities of the compositions may be reduced by inclusion, as desired, of liquid or more fluid monomers. Such two-component systems polymerise rapidly when mixed in suitable proportions.

The polymerisation reaction of the compositions generally requires up to about ten minutes after activation by heating or acidification. In some instances the polymers may be of relatively low molecular weight and be soluble in various organic solvents; other compositions gel in as little as 2 minutes after acidification or warming, and provide high yields of high molecular weight polymer. Polymerization of compositions of the invention in the presence of air is distinctive in that substantially no layer or puddle of monomer remains on the surface, although the outer surface may be slightly tacky in some instances. In many instances, e.g. in filling cavities in teeth excess polymer, including any slightly tacky surface which may be present, is cut away in finishing operations.

The present invention includes polymerisable compositions of value for dental fillings which have good adhesion to tooth structure and have desirable thermal expansion characteristics. The incorporation of fillers such as those comprising spheroidised lithium aluminium silicates, provides dental filling compositions having desirably controlled thermal expansion characteristics. These dental fillings are described in our co-pending Patent Application No. 58597/67 (Serial No. 1,113,723).

For dental purposes, acidification is presently preferred for activation of the compositions, as is the use of two component systems.

As stated hereinabove heat or acids initiate or activate the polymerisation. Generally, heating to temperatures of the order of 80 to 100°C for about 10 minutes and often much less is sufficient. Such temperatures are sufficiently high to effect at least partial dissociation of the triaryl borane complex.

Alternatively, acidic materials such as acrylic acid, methacrylic acid, maleic acid, phosphoric acid, acetic acid, trifluoroacetic acid, and *p*-toluene sulphonic acid, (which for convenience may be pre-dissolved in a further amount of monomer) are mixed in rapidly. In such systems the monomeric acids which participate in polymer formation, e.g. maleic, citraconic, acrylic and methacrylic acids are preferred, and such polymerised compositions exhibit better and more prolonged adhesion when the cured composition is under prolonged exposure to moisture. Although any acid will activate the compositions of the invention, including inorganic acids, the most useful results are obtained using as the acid, acrylic or methacrylic acid.

The following Examples illustrate compositions of the invention and methods for their preparation and use. In these Examples all parts are by weight unless otherwise specified.

## EXAMPLE 1.

A composition of the invention (mixture A) is prepared by mixing 100 parts of fusel oil acrylate, 2 parts of benzoyl peroxide and 3 parts of triphenyl borane-ammonia complex. Control mixtures are prepared each from 100 parts of the same fusel oil acrylate monomer with 2 parts of benzoyl peroxide (mixture B), and with 3 parts of triphenyl borane-ammonia complex (mixture C), respectively. Portions of each of A, B and C are heated in the presence of air at 82°C for 10 minutes. The two control mixtures (B and C) show no reaction and remain fluid. The composition of the invention (A) is polymerised to a tacky polymer which is slowly soluble in ketones such as methyl ethyl ketone and is suitable for use in adhesives.

## EXAMPLE 2.

This Example illustrates an embodiment of the invention in which the monomer is combined with the triaryl borane-complex as one component and the catalyst is then added simultaneously with an activating acid as a second component. The composition can be polymerised directly and does not suffer from the inhibitory effect of air. The inhibitory effect of air and/or oxygen varies for different monomers and probably for the time and manner of exposure; that is, the degree of aeration of the monomer which may depend e.g. upon pouring from the container in slightly different ways, exposure to air for slightly different periods or ability to dissolve oxygen.

A series of polymerisations illustrative of this embodiment of the invention are carried out employing as a first component 50 parts of monomer to which is added 1 part of different triarylborane-complexes.

The first component is a mixture of 37.5 parts of the glycidyl methacrylate adduct of bisphenol A (prepared by reacting 1 mole of bisphenol A with 2.1 moles of glycidyl methacrylate in the presence of about  $\frac{1}{2}$  weight percent of N,N-dimethyl-p-toluidine at about 60°C for 36 hours. It is used as prepared, i.e. without purification, and thus contains approximately 1 percent of oxirane oxygen and unremoved N,N-dimethyl-p-toluidine, and 12.5 parts of methyl methacrylate to which is added 1 part of triaryl-borane complex, the complex being pre-dissolved in the methyl methacrylate prior to admixture with the adduct monomer.

The second component in each instance is 2 parts of a 5 percent by weight solution of benzoyl peroxide in methacrylic acid.

The first and second components were mixed together and poured into small aluminium weighing dishes under aerobic conditions, i.e. they were exposed to the atmosphere. In a few minutes at room temperature a disc of polymer formed, and after 12 hours the disc was removed from the dish, weighed, and any unreacted monomer and/or low molecular weight polymers and oligomers were extracted from the disc using methyl ethyl ketones. The weight of the residue (recorded as percent of original weight) is a measure of the extent of cross-linking and polymerisation to high molecular weight polymer.

Table 1 shows the yields of insoluble polymer obtained when using different complexes of triphenyl borane.

TABLE 1

Complexing Agent	Total Weight at 12 hours	Yield (Insoluble polymer)
NH <sub>3</sub>	99	96
N(CH <sub>3</sub> ) <sub>3</sub>	99	96
C <sub>12</sub> H <sub>25</sub> NH <sub>2</sub>	98	91
Pyridine	96	81

Table 2 shows the results of otherwise identical procedures except that complexes of various bases with other triaryl boranes were used.

TABLE 2

Complex	Total Weight at 12 hours	Yield
$(p\text{FC}_6\text{H}_4)_3\text{B} \cdot \text{NH}_3$	94	77
$(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{B} \cdot \text{Pyridine}$	91	74
$(1\text{-naphthyl})_3\text{B} \cdot \text{NH}_3$	94	73
$  \begin{array}{c}  \text{CH}_3 \\    \\  (p\text{FC}_6\text{H}_4)_3\text{B} \cdot \text{H}_2\text{N}-\text{C}-\text{CH}_2\text{OH} \\    \\  \text{CH}_3  \end{array}  $	90	70
$(p\text{C}_2\text{H}_5-\text{C}_6\text{H}_4)_3\text{B} \cdot \text{Pyridine}$	90	66
$(p\text{FC}_6\text{H}_4)_3\text{B} \cdot (\text{CH}_3)_2\text{N}-\text{CH}_2-\text{CH}_2\text{OH}$	93	61

When these tests are run at somewhat elevated temperatures with greater dissociation and solubility of the complexes, the yields of insoluble polymer are higher and there is less formation of low molecular weight soluble polymer. Part of the variation in results observed is believed due to the difficulty of dissolving certain of the complexes so that they may actually continue to hinder the reaction through failure to dissociate and/or to react with the methacrylate acid before that has entered into the polymer molecule. A further reason for the lower yields of higher molecular weight polymer may be due to formation of lower molecular weight solvent-soluble polymer molecules. When the composition is to be employed for purposes of embedding or encapsulation or the like purposes it is preferred to employ systems which proceed to very high yields of high molecular weight polymer. Such compositions include as nitrogenous base complexes those complexes in which the base is an aliphatic amine or ammonia.

It should be noted that the N,N-dimethyl-p-toluidine associated with the adduct of bisphenol A portion of the first component is known as an accelerator for "self-curing" dental resins, see Skinner and Phillips, *The Science of Dental Materials*, W. B. Saunders Co. Philadelphia U.S.A. (1960) page 170.

When a control sample otherwise identical to the above 2 component systems except for the omission of any triaryl borane base complex is used, the yield of insoluble polymer is about 75 percent and a puddle of liquid remains on the surface. Furthermore, the gel-time is generally longer, as illustrated in the next Example.

#### EXAMPLE 3.

A series of tests similar to those described in Example 2 above are run, except for the substitution in the first component of ethylene glycol dimethacrylate with 1 percent dimethyl p-toluidine as an auxiliary accelerator in place of the bisphenol A derivatives. The same proportions are used. The time to gel-formation at room temperature (about 25°C) after mixing the components was recorded. In the absence of the triaryl borane complex, control specimens require about 5 minutes to gel. The gel-time for compositions containing different complexes is shown in Table 3. When elevated temperatures are employed, times to gelation are generally less. More rapid gelation, i.e. setting, is important in many instances, such as in dental resins. For such purposes, of course, elevated temperatures may be impractical and the accelerated gel-time attainable in compositions of the invention is therefore valuable.

TABLE 3

Complex	Gel Time in Minutes
(1-naphthyl) <sub>3</sub> B. Benzene	2.25
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> B. Pyridine	2.5
(pCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> B. Pyridine	2.5
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> B. NH <sub>3</sub>	3
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> B. N(CH <sub>3</sub> ) <sub>3</sub>	3
(pFC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> B. H <sub>2</sub> N—C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> OH	5

## EXAMPLE 4.

Compositions of the invention modified to be particularly suitable for use as two-component dental resins suitable for filling cavities in teeth, may be prepared by adding a filler intended to match the properties and colour of natural teeth. Suitable filler materials include 325 mesh silica or alumina powder (particle size of less than 0.0017 inch (43 microns) (diameter) and synthetic fluorapatite. This latter material is prepared by sintering stoichiometric amounts of CaF<sub>2</sub> and tribasic calcium phosphate at 1100°C for a period of 4 hours and reducing the particle size to pass a 325 mesh Tyler sieve (which has 43 micron openings). Traces of suitable tinting agents are incorporated as desired. The properties of the fillers may be modified for firm bonding into the resin structure as by treatment with tris-(2-methoxyethoxy) vinyl silane.

## EXAMPLE 5.

This Example illustrates benefits attainable for dental purposes from compositions of the invention.

The monomer employed is the bisphenol A bis(glyceryloxy) methacrylate described in Example 2 as the adduct of bisphenol A and glycidyl methacrylate. The viscous monomer (containing oxirane oxygen and N,N-dimethyl-p-toluidine) was diluted with 15 percent by weight of methyl methacrylate to lower the viscosity.

In the following Table 4 Composition A is according to the invention and Compositions B and C are comparative examples.



TABLE 4

Composition (parts of each)	A	B	C
85:15 Monomer adduct: methyl Methacrylate	100	100	100
(including N,N-dimethyl-p-toluidine)	1	1	1
Triphenylborane-NH <sub>3</sub> complex	0.5	—	—
Catalyst			
Benzoyl peroxide	0.1	0.1	1.25
Methacrylic acid	10	10	—
Bulk gel time (min.)	1—1.5	1—1.5	5—8
Film gel time covered	same	same	same
Film gel time exposed	1.5—2.0	Inhibited	Inhibited
Tensile adhesion (in teeth)	1200 psi	1200 psi	400 psi

5 The above compositions were compared on the basis of time for polymerisation of a 5 gram sample of each in a 1.5 inch diameter aluminium dish (designated as bulk gel time); time for polymerization of a 0.002 inch thick coating which was protected from the air by a laminated sheet of polyethylene terephthalate polymer and metal foil, (film gel time covered) and another .005 cm thick coating uncovered (exposed). 5  
 10 The tensile adhesion test measured the strength of bond of a threaded aluminium dowel .060 inches in average diameter cemented into a 0.064 inch hole drilled in a human tooth. For purposes of testing, the teeth (obtained from a dental clinic) were maintained moist and swabbed dry immediately before use in the test. Polymerisation temperature was about 25°C. 10

The inhibitory effect of air in aerobic polymerisation is overcome by inclusion in Lot A of triphenylborane-ammonia complex.

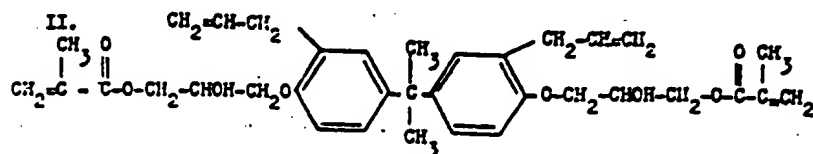
15 A composition somewhat similar to composition C in Table 4 has been described (R. L. Bowen and M. S. Rodriguez, J. Am. Dental Association Vol. 66, page 378, March, 1962) which differs in containing no free oxirane oxygen. In that system excess bisphenol A is reacted with glycidyl methacrylate in an inert atmosphere and the excess bisphenol is then removed by extraction with 5 percent aqueous NaOH followed by water washes. Other methods of preparing an adduct which is free from oxirane oxygen are described in United States Patent No. 3,066,112. Such oxirane-free systems are, of course, incapable of providing the interpenetrating reticulate structures obtained from compositions of this invention which contain oxirane oxygen. 20

#### EXAMPLE 6.

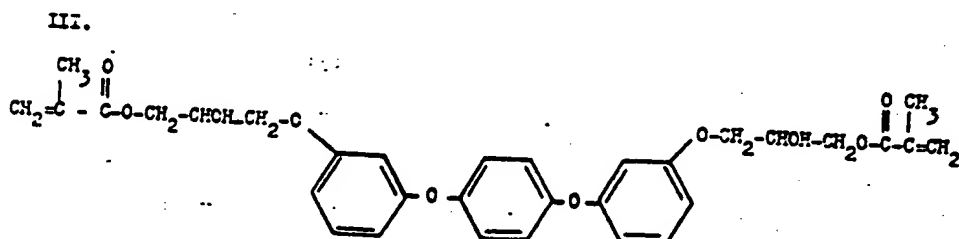
25 This Example illustrates the effect of triphenyl borane-ammonia complex on the aerobic polymerisation of several acrylate-type monomers. 25

30 Aluminium nails with 0.25 inch diameter heads are washed with acetone and then bonded head to head by polymerisation of the monomers in situ for about 16 hours at 35°C. In order to obviate the variation of strength with time, the longer period of polymerisation is employed for purposes of these test samples even though polymerisation is substantially complete in less than 20 to 30 minutes. Table 5 shows the tensile strengths achieved using four different monomers. In each sample, in addition to the indicated monomer, the composition of the invention included, in weight percent, 3 percent benzoyl peroxide, 1.5 percent triphenyl borane-ammonia complex and 0.1 percent N,N-dimethyl-p-toluidine activator. The control samples were identical except for omission of the triphenyl borane-ammonia complex. 35

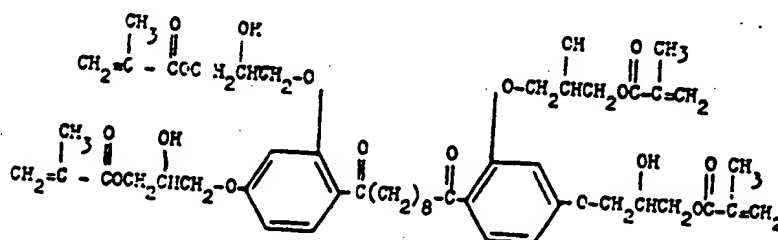




3,3'-diallyl-bisphenol A-glycidyl methacrylate adduct.

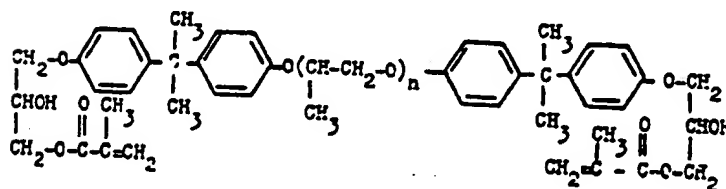
1,4-bis(*m*-[methacryloxy glyceroxy] phenoxy) benzene.

IV.



Sebacyl-bisresorcinol-glycidyl methacrylate adduct.

V.



The bisphenol A bisether-glycidyl methacrylate adduct of polypropylene glycol, *n* having an average value of about 7, when prepared from polypropylene glycol having an average molecular weight of 425.

It will be seen that acrylates of this type prepared from higher polyethylene and polypropylene glycols may contain up to about 100 carbon atoms or more. Also each of the prepolymers I to V contains about 1 percent of oxirane oxygen and 0.9 percent of *N,N*-dimethyl-*p*-toluidine because of the procedure employed in making the same.

Compositions of the invention are prepared as described in Example 2 above employing any one of the above prepolymers I to V combined with 1 percent by weight of triphenyl borane-ammonia complex and 10 weight percent of methyl methacrylate as the first component and using a 5 percent by weight solution of benzoyl peroxide in methacrylic acid as the second component. Each first component (100 parts) is mixed thoroughly and rapidly with 4 parts of the peroxide-containing methacrylic acid-component and immediately applied to the flat surfaces at the long edges of a pair of 7 × 7 inch aluminium sheets or panels (which had previously been cleaned

and etched according to United States military specification MIL-A-5090B). Each pair was overlapped by one-half inch and permitted to polymerise under a light pressure (about 10 p.s.i.) for 5 to 10 minutes. The pressure was then released and the panels allowed to stand for a further one to three days. Six sets of test panels were prepared this way. The beads of exuded polymer at the overlapping joints were cut away and the panels were sawed into test strips 1.0 inch wide. The strengths of the bonds were determined in an Instron (registered Trade Mark) tester at various temperatures, and at 24° C after exposure to 100 percent relative humidity at 54.4°C for up to 60 days. Each sample was maintained at temperature for 20 minutes before testing. Results in pounds per square inch are shown in Table 6. When the tests were repeated, the results were usually within about 10 percent of the average, occasionally to within 15 percent.

TABLE 6

Prepolymer composition	I	II	III	IV	V
Temperature in °C.	Tensile in psi				
-55	500	420	500	800	320
+24	810	1300	1180	1240	1250
+82	1920	530	3500	—	1320
+121	1570	—	1250	—	—
+149	920	—	1040	—	—
Exposure (days)					
15	1070	1110	1340	1690	1000
30	1170	870	1250	720	—
60	1180	—	—	—	1180

The dashes (—) indicate that no test was made of that sample. The adhesion of compositions I and V after 60 days exposure to 100 percent relative humidity is particularly outstanding as are also the strengths of bonds of compositions I and III at elevated temperatures.

## EXAMPLE 9.

Compositions of the invention may include other diluent monomers to enhance fluidity, and an activating monomeric acid. This Example and Example 10 serve to show variations in these constituents, specific illustrative diluent monomers such as ethyl acrylate being specifically mentioned in Table 7 hereinafter.

Two component compositions are prepared using prepolymer I of Example 8 (which includes about 1 percent oxirane oxygen as glycidyl methacrylate and 0.9 percent N,N-dimethyl-p-toluidine). The actual molar composition for each component being as follows:

Component 1	Moles
Prepolymer I adduct (which includes glycidyl methacrylate and N,N-dimethyl-p-toluidine)	0.0032
	0.00113
	0.00015
Diluent monomer	0.0007 to 0.002
Triphenyl-borane-ammonia complex	0.00008

Component 2	Moles
Methacrylic acid	0.00142
Diluent monomer	0.0001 to 0.00032
Benzoyl peroxide	0.00003

The amount of diluent monomer is varied in the samples so that levels of 10, 20 and 30 mole percentage of the total composition are used.

For component 1 of the several compositions, about 0.02 gram of triphenyl borane-ammonia complex is dissolved in 0.0007, 0.0014 and 0.0020 mole of the diluent monomer to provide the respective 10, 20 and 30 mole percent levels, and the solutions are added to 1.8 g of the prepolymer I (which includes the glycidyl methacrylate and N,N-dimethyl-p-toluidine). The components 2 are made by adding 0.00010, 0.00020 and 0.00032 mole respectively of diluent monomer to 0.13 g of a solution of 0.50 g of benzoyl peroxide in 8.0 g of methacrylic acid. The components 1 and 2 of each respective composition were blended and applied to aluminium panels as described in Example 8 and test pieces were prepared as there set forth. Overlap shear strengths were determined at various temperatures and after exposure to 100 percent relative humidity at 54.4°C for 30 days. The results in pounds per square inch of overlap are set out in Table 7, the figures under "30 day exposure" being determined at 24°C after the exposure for that time to 100 percent relative humidity.

TABLE 7

## Overlap Shear

Diluent monomer and level	24°C	82°C.	121°C.	30 day exposure
Mole % Ethyl Acrylate				
10	660	1600	1160	920
20	780	1310	1070	940
30	830	1480	1000	1050
Mole % n-Butyl Acrylate				
10	820	1280	1200	1020
20	870	1230	950	1140
30	930	1220	720	1170
Mole % Isooctyl Acrylate				
10	520	980	370	1280
20	1060	710	370	1020
30	1100	720	250	1040
Mole % Phenyl Acrylate				
10	490	980	720	—
20	1060	800	430	—
30	1180	420	240	—
Mole % Acrylonitrile				
10	820	1490	1160	880
20	1080	1555	1160	1060
30	790	1180	620	1140
Mole % Methyl methacrylate				
10	600	1840	1020	950
20	980	1990	990	1560
30	970	1720	970	920
Mole % Hexyl methacrylate				
10	770	1520	1060	1110
20	640	1560	960	1220
30	1420	1270	650	1040
Mole % Hydroxethyl methacrylate				
10	770	1270	730	—
20	810	1580	1010	970
30	640	1460	840	940

## EXAMPLE 10.

The amount of monomeric acid employed in the compositions also is found to cause some variation in properties. Tests similar to those described above are conducted using different amounts of acrylic and methacrylic acid. The first component consisted of 90 parts of Prepolymer I of Example 8 (which includes excess oxiranic oxygen as glycidyl methacrylate and N,N-dimethyl-p-toluidine as before), 10 parts of methyl methacrylate and 1 percent by weight of triphenylborane-ammonia complex. The second component of the composition consisted of 80 parts of monomeric acid, 20 parts of methyl methacrylate and 5 parts of benzoyl peroxide. The total percent of monomeric acid (and simultaneously of catalyst) was varied by employing different amounts of the second component, viz. 4, 8 and 12 drops for each 2.0 g of Component 1 (corresponding to about 7, 14 and 20 percent by weight respectively of monomeric acid). Tests are conducted as in Example 9 and also with 60 days exposure to 100 percent relative humidity. The results in pounds per square inch of overlap are set forth in Table 3.

TABLE 8

Monomeric acid and level	Overlap Shear				30 days exposure	60 days exposure
	-55°C.	24°C.	82°C.	121°C.		
Acrylic acid in %						
7	—	1100	1580	1480	1300	1300
14	590	2000	2080	1860	1630	1330
20	850	2280	2220	1860	2040	1660
Methacrylic acid in %						
7	510	830	1320	1620	1140	940
14	370	880	1440	1390	1260	1680
20	400	760	1580	1660	1360	1120

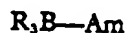
All the above compositions are found to retain appreciable strength (upwards of 800 p.s.i.) even at 149°C, this property apparently improving with increasing amount of methacrylic acid. It is found that when non-monomeric (with respect to the acrylate polymerisation) acids are employed in similar compositions, there is substantially no retention of adhesive strength on exposure to 100 percent relative humidity as in the above test. Among such non-monomeric acids which give poor results in this test, are certain strong acids such as trifluoroacetic, sulphuric and phosphoric acids and certain relatively weaker acids such as acetic, p-toluene sulphonic and pyromellitic acids.

Testing of compositions of the invention for adhesion to teeth as a measure of their value in dental resins is very much complicated by the mechanical difficulties of obtaining a sound tooth surface free from fragments and fissures. This is illustrated by the variation in results obtained in duplicate tests. Five human teeth preserved moist having sound portions are drilled with holes 0.060 inch deep and 0.064 inch in diameter with the sides converging at an 8° angle. Threaded tapered stainless steel pins 0.051 inch in diameter are cemented in the center of each hole employing a composition of the invention, Component 1 consisting of 80 parts of the adduct of glycidyl methacrylate and bisphenol A (freed from amine and oxirane oxygen), 10 parts each of glycidyl methacrylate and methyl methacrylate, 0.7 part of N,N-dimethyl-p-toluidine and 1 part of triphenyl borane ammonia complex. For each gram of Component 1, 2 drops of a 5 percent by weight solution of benzoyl peroxide in a mixture of 20 parts methyl methacrylate and 80 parts of methacrylic acid was used as the activator. Rapid manipulation is required, as in dental operations, because of the prompt gelling of the composition. After polymerisation has proceeded for about 10 minutes, the excess bead of polymer was cut away and the tooth with implanted peg is aged for 4 weeks at 37°C in 1 normal sodium chloride solution. The pins are then pulled from the tooth using an Instron tester and the force necessary to do so is

expressed in pounds per square inch. The values on the five samples are 954, 1062, 1388, 1757 and 2075 psi, respectively. The spread of values found is believed to be an indication of variation in the test teeth per se. It appears that the actual value should be in the range of 1700 to 2000 psi. Clinical trials of similar compositions of the invention, but including fillers to match tooth colouring show excellent adhesion to tooth surface over prolonged periods in spite of the mechanical stress induced by mastication and the presence of moisture.

#### WHAT WE CLAIM IS:—

1. A composition activatable in the presence of a free-radical catalyst to polymerise under aerobic conditions comprising one or more mono- and/or bis-acrylate and/or methacrylate monomers and blended therewith from 0.05 to 6 percent by weight of the monomer or monomers of a triaryl borane complex, the acrylate or methacrylate monomer or monomers being ones which in the absence of the complex are polymerised with difficulty by free-radical initiators except in the almost complete absence of oxygen and the complex having the general formula:



in which R represents an aryl radical having from 6 to 12 carbon atoms, and Am represents sodium hydroxide, ammonia, benzene or an amine.

2. A composition as claimed in Claim 1 which contains sufficient oxirane group containing monomer to give an oxirane oxygen content of from 0.5 to 2.0 percent by weight of the composition.

3. A composition as claimed in Claim 1 or Claim 2 in which the aryl radical in the borane complex is phenyl.

4. A composition as claimed in any preceding claim in which the borane complex has been formed between a triaryl borane and a primary, secondary or tertiary alkylamine, a cycloalkylamine, and alkanolamine, a primary aralkylamine, an alkylene polyamine or a secondary or tertiary heterocyclic amine.

5. A composition as claimed in any preceding claim which is storable and heat or acid activatable, in which a free-radical catalyst is present in the composition in an amount of from 0.01 to 5 percent by weight of the monomer, and the catalyst is a peroxide polymerisation catalyst.

6. A composition as claimed in Claim 5 in which the amount of peroxide polymerisation catalyst is from 0.01 to 2 percent by weight of the monomer.

7. A composition as claimed in any preceding claim which additionally contains from 0.5 to 2 percent by weight of a nitrogenous base having a pK value of not more than 10 and a molecular weight of from 30 to 800.

8. A composition according to Claim 1 and substantially as herein described in any Example.

9. A kit containing all the components of a composition as claimed in any preceding claim in at least two discrete containers, the components being distributed among these containers in such a way that the composition is stable until the components from the containers are mixed.

10. A process for initiating the aerobic free-radical polymerisation of a composition as claimed in any of claims 1 to 8 which contains a free-radical initiator, comprising heating the composition to decompose the complex or adding acid to the composition to decompose the complex.

11. A process as claimed in Claim 10 in which the composition includes sufficient oxirane-group containing monomer to give from 0.5 to 2.0 percent by weight of oxirane oxygen, and the initiation of the polymerisation of the composition is effected by adding a co-monomeric acid.

12. A process as claimed in Claim 11 in which the co-monomeric acid is acrylic acid or methacrylic acid.

13. A process according to Claim 10 and substantially as herein described.

14. The polymerised material resulting from the polymerisation of a composition as claimed in any of claims 1 to 8 by a process as claimed in any of claims 10 to 13.

For the Applicants:

LLOYD WISE, BOULY & HAIG,

Chartered Patent Agents,

Norman House, 105—109 Strand, London, W.C.2.